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BURN RATE MODIFICATION WITH CARBORANE POLYMERS

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U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND
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Picatinny Arsenal, New Jersey

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14. ABSTRACT <p>In the past, propellants containing boron clusters like n-hexyl carborane demonstrated an improved burn rate, decreased pressure exponent, and maintained a high energy output. However, the technology was hampered by expensive and hazardous synthesis as well as migration issues of the n-hexyl carborane plasticizer. A new, affordable synthesis procedure of decaborate salts was established at the University of Missouri-Columbia, which provides material for alkylation and subsequent synthesis to carboranylmethyl acrylate. In this paper, the investigation of the integration of covalently-bonded boron achieved through copolymerization in various binder polymers is presented. Since pure carboranylmethyl acrylate polymer is a solid crystalline material at room temperature, it was co-polymerized to produce a material suitable for formulations. The co-polymerization investigated was a combination of carboranylmethyl acrylate, butyl acrylate, and 2-hydroxyethyl acrylate. The boron-rich carborane was intended to serve as the high energy fuel portion of the polymer, the butyl acrylate provided a glass transition temperature below room temperature and low viscosity, and the hydroxylethyl acrylate contributed a cross-linkable moiety. The resulting polymer was used in a cast-cure formulation containing aluminum and ammonium perchlorate in order to test the effect of the carborane additive on the formulation burn rate when compared to a hydroxyl-terminated polybutadiene baseline. Strand burn rate testing demonstrated a distinctive increase in the burn rate for the carborane containing formulation. Synthesis and characterization of the carborane-based polymer are discussed along with the designed formulation. Further test data including sensitivity and thermal characterization are presented.</p>					
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SUMMARY

Advances in the field of borate research have resulted in a novel polymer that serves to enhance the burn rate of high performance rocket propellants. With funding support from the U.S. Army, the Center for Borane Technology at the University of Missouri (ref. 1) developed a safer, cheaper synthesis process for borate salts. Through proprietary synthesis techniques, the university converts the borate salt into a carboranylmethyl acrylate monomer. Research efforts at the U.S. Army Armaments Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, NJ, have incorporated this high energy moiety into a novel co-polymer with a glass transition temperature below room temperature as well as hydroxyl functionality. This co-polymer was used as a cast cure type binder system yielding an increase in the burn rate of an ammonium perchlorate (AP)/aluminum (Al)-based rocket formulation. While additional characterization and optimization are required for full understanding of the synthesized co-polymer, preliminary testing showed that carborane containing polymers is a viable candidate for enhanced rocket performance or other propellant applications. Future optimizations of polymer and final formulation mechanical properties while considering performance measures would provide a superior propellant material.

INTRODUCTION

Boron additives in propellant formulations can alter the burn rate and pressure dependence of the propellant. Carborane derivatives have been selected for this application because of their ability to provide boron in a nonoxidized form covalently bonded to the binder's polymer backbone in a random co-polymer with a structure similar to figure 1.

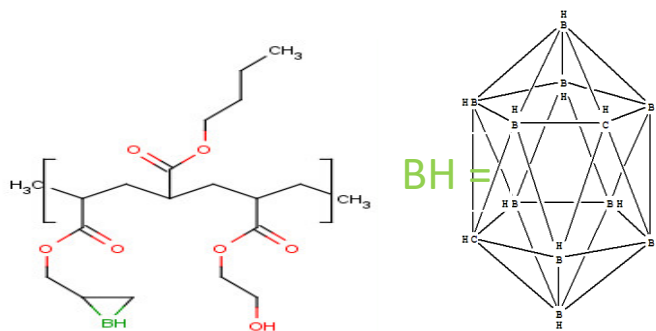


Figure 1

Co-polymer structure including carboranylmethyl acrylate, butyl acrylate, and 2-hydroxyethyl acrylate

The co-polymers designed have varied ratios of the acrylate monomer units shown in order to achieve a final polymer with a glass transition (T_g) below room temperature and the capability of reacting with isocyanates to form urethane cross-linking.

BACKGROUND

Development of boron-containing propellant systems has long been hindered by the kinetic restriction of boron oxide layers on the surface of bulk boron powder (ref. 2). The use of borate-type materials may help increase the oxidation kinetics that could offset the kinetics of hydrogen borate/boric acid (HOB) formation. The structure and stability of a carborane cage is also advantageous over boron powders because it does not have a glassy boron oxide layer at ambient or burn conditions. Dispersion of the boron atoms into the physical space of a carborane cage allows for the boron to be more readily accessed during combustion, which favors the rapid

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formation of HOB₂O and B₂O₃. This rapid oxidation releases all of the potential energy achievable from boron combustion in a manner that enhances the burn rate of high performance propellants without the delay of melt or diffusion limitations. Carboranes have been used in this manner in previous works to enhance the burn rate and reduce the pressure exponent of propellant systems (refs. 3 and 4). Unfortunately, the only material available for this application was cost prohibitive n-hexyl carborane (NHC). While NHC was a capable plasticizer in hydroxy-terminated polybutadiene (HTPB)-based binder systems, it exuded from the final formulations and was ultimately deemed ineffective. The novel polymer presented in this work solves both of the issues with NHC while maintaining its performance advantages.

The production of carboranes originally began by reacting sodium borohydride with a catalyst to form decaborane. This intermediate material is both volatile and toxic and had to be isolated for input into subsequent steps. Two additional steps, one containing acetylene, were then required to achieve carborane (C₂B₁₀H₁₂). Due to both materials' risk and processing, this production technique could not be used to produce large enough quantities of material necessary for large-scale applications. Recently, U.S. Army-sponsored research conducted at the University of Missouri has resulted in a novel synthetic route that avoids isolation of hazardous intermediates and drastically reduces the processing time and cost of production (ref. 1). With this new technology, boranes and subsequent carborane materials are supplied safely, in a scalable route, and with reasonable cost.

Consistently and safely produced carborane starting material led to collaboration between ARDEC and the University of Missouri to develop a material that sought to eliminate the issues associated with NHC. By synthetically producing an acrylate monomer from carborane, one could incorporate the carborane cage covalently bonded to the binder matrix, which would eliminate migration out of the propellant binder. Unfortunately, poly(carboranylmethyl acrylate) was discovered to be crystalline at room temperature, excluding the homo-polymer from solids loading applications. However, because acrylate monomers are easily initiated with azobisisobutyronitrile (AIBN) and undergo free radical polymerization, the carboranylmethyl acrylate could be co-polymerized with any type of acrylate monomer (ref. 5). With casting applications in mind, butyl acrylate and 2-hydroxyethyl acrylate were selected as co-polymers with the carboranylmethyl acrylate. The hydrocarbon-rich butyl acrylate would serve as a glass transition temperature reducer that would flow for solids loading. The 2-hydroxyethyl acrylate was chosen because of its hydroxyl functionality, which would allow curing with common isocyanates in the presence of a catalyst (ref. 6). Polymerizations and subsequent characterization are the focus of this paper. The end goal was a boron-enhanced cast cure propellant binder with none of the previously experienced complications of exudation.

TEST METHODS

Materials

Carboranylmethyl acrylate monomer was obtained from the University of Missouri at Columbia. Toluene, methanol, AIBN, butyl acrylate, 2-hydroxyethyl acrylate, isophorone diisocyanate, and dibutyltin dilaurate were purchased from Sigma-Aldrich, St. Louis, MO. Co-polymers containing 0 and 10% boron by weight were synthesized at ARDEC. Co-polymers were used without further purification and analyzed by low temperature differential scanning calorimeter (DSC) and Fourier transform infrared (FTIR). The H30 AI was provided by Valimet, Inc., Stockton, CA. The AP was provided by John Bolognini and Joseph Laquidera at ARDEC.

Synthesis of Co-polymers

All polymer products synthesized were created following the same one-pot procedure. Dry toluene was charged to a three-neck flask. Allotted monomers were added to the flask. Stirring was initiated, and the temperature was maintained at 65°C. A flow of nitrogen gas was run through the system in order to create an inert atmosphere. The AIBN was placed in a separate dry toluene solution. The AIBN solution was added drop wise to the monomer solution at a slow rate resulting in radical initiated polymerization (ref. 4). An aliquot of toluene was used to wash the addition funnel into the reaction flask. Once addition was complete, the flask was sealed with a nitrogen blanket and allowed to mix at 65°C overnight (minimum 15 hr). The resulting polymer solution was crashed out in cold methanol. Solvent was evaporated and the resulting clear polymer was dried in a 60°C vacuum oven (%Y = 95 to 100). Polymers were evaluated through low temperature DSC and FTIR. Spectra can be seen in appendix A.

Gum Stocks

Gum stocks of the resulting polymers were created using isophorone diisocyanate (IPDI) as a curative and dibutyltin dilaurate as a catalyst. Curing was confirmed by the gum stock's rubbery consistency and time elapse FTIR. Spectra can be seen in appendix A.

Formulation

Due to the unique nature of the synthesized polymer, a modified baseline formulation was used. The rocket assist M913 105-mm projectile propellant was selected as a model formulation from which core materials ratios were maintained through this iteration of testing. Specifically, the AP/Al ratio was maintained as well as the bimodal mix of particle sizes within the AP fraction of the mix. Binder, curative, catalyst, and other additives were altered in order to achieve a viscosity that was safely processed on the small scale until safety data and proof-of-concept was achieved. Due to the uncertainty associated with the novel materials used, only small-scale polymer syntheses and subsequent formulation mixes were performed. All formulation ratios were maintained across the three tested polymers in order to isolate variation in results to a single variable: polymer composition.

A counter centrifugal SpeedMixer™ was used to create small-scale mixes of the desired formulations (see appendix B, table B-1). Mixing was initiated with polymer and plasticizer materials alone to create a lacquer in the mixing vessel. Solids were added gradually in order to ensure uniform distribution and optimal coating. In general, speeds and mix times were increased in order to increase the sheer present in the sample as additional solids were incorporated causing the viscosity to increase. Once a uniform distribution was observed, a curing agent and catalyst were added, and the materials were mixed under vacuum to remove porosity. The Explosive Research Laboratory impact test, Bundesanstalt fur Materialprufung (BAM) friction test, ARDEC electrostatic discharge test, and DSC analysis of the small-scale runs were performed to ensure the products were safe to handle. Once safety thresholds were verified, final products were cast into molds for rate sticks and cured in a 60°C oven overnight. Cured rate sticks were removed from molds, bulk materials were analyzed via DSC for stability, and sticks were evaluated in burn rate testing. Spectra and burn rate results can be seen in appendix B.

Analysis

The DSC spectra were recorded from a Perkin Elmer DSC 4000. The temperature was increased from 40° to 450°C at a rate of 5°C/min.

Infrared absorption data was recorded as thin films deposited on a NaCl plate on a Perkin Elmer Spectrum 100 FTIR in the range of 650 to 4,000 cm^{-1} at ambient temperature and analyzed using Perkin Elmer Spectrum software.

Rate sticks were coated with a thin film burn rate inhibitor to ensure uniform burn down the length of the stick. Burn rates were recorded with a Design Integrated Technology strand burner at three different chamber pressures: 750, 1500, and 3000 psi.

RESULTS

Two new co-polymers were successfully synthesized through a one pot procedure: one containing 0% boron and the other containing 10% boron by weight. Both polymers were collected in high yield. The FTIR spectra confirming the incorporation of the various monomer functionalities are shown in appendix A. The state of the clear polymers can be considered sticky and highly viscous but free flowing at room temperature.

A successful polymer synthesis was confirmed through the analysis of FTIR spectra (app. A, fig. A-2) acquired for the co-polymers. Key peaks present in both polymers correspond to the hydroxyl functionality and the hydrocarbon functionality located around 3,500 cm^{-1} and 2,959 cm^{-1} , respectively. The hydroxyl peak is extremely low in intensity due to the minimal amount included in the synthetic design. The peak located around 2,590 cm^{-1} was only seen in the polymer that contained the carboranylmethyl acrylate monomer, indicating the presence of the carborane cage. This confirmed the successful incorporation of covalently-bonded boron into the polymer matrix. Low temperature DSC spectra confirmed the physical observation that the polymers flow freely at room temperature. As seen in appendix A, the spectra show a T_g for the 0% boron co-polymer as -69.41°C and the 10% boron co-polymer as -69.36°C.

Gum stock analysis of the 10% boron co-polymer was performed in order to confirm the necessary reactivity with the IPDI as well as mechanical properties capable of holding propellant rate sticks together. Mechanical properties were not actually measured quantitatively due to a limited amount of material, but observations confirmed the rubber consistency necessary for formulation. The chemical reaction resulting in the urethane formation was tracked through time elapsed FTIR. The spectra from that study can be found in appendix A.

Strand burning tests were administered on three different formulation samples in order to provide an unbiased evaluation of the novel polymer. First, an HTPB formulation based on the altered values was tested to provide a comparative baseline to current technology. Second, a carborane-free acrylate polymer was synthesized and used as an "inert" polymer in the same formulation. This provided a more direct baseline, which proved that any alterations in burn rate were due to the carborane, not the novel acrylate backbone structure. Third was the carboranylmethyl acrylate containing polymer, which calculated at 1.14% boron in the overall formulation. Plotted results from the strand burning of these three formulations at three pressures are shown in figure B-3 of appendix B. It was evident that the carboranylmethyl acrylate containing polymer possessed the fastest burn rate at all pressures.

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CONCLUSIONS

Carboranylmethyl acrylate can successfully be incorporated into a cross-linkable random co-polymer with a glass transition below room temperature. The resulting polymers sufficiently serve as a binder matrix for ammonium perchlorate/aluminum-based cast cure propellant formulations. Propellant rate sticks created from the formulations incorporating carborane-containing polymers demonstrate superior burn rates at three different test pressures.

RECOMMENDATIONS

Due to the limited quantity of the synthesized co-polymers, only preliminary testing and characterizations were performed. It is anticipated that with scale up and higher shear mixing, less deviation in burn rate data would be obtained. Extensive work could uncover the full potential of these novel materials. This technology is currently being developed on various levels for additional proof-of-concept. Full characterizations of the polymers that have been produced to date are still in progress. Additionally, alternate acrylate monomers that may affect the performance as well as the mechanical properties of these materials have not been fully investigated. Finally, a design-of-experiments driven optimization of the monomer ratios within the co-polymers balanced with the various energetic fill materials available would result in a propellant worthy of scale up and evaluation of more higher resolution tests such as shock sensitivity, large strand burn rates, and closed bomb testing.

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APPENDIX A
CO-POLYMER DATA: FOURIER TRANSFORM INFRARED (FTIR) SPECTRA, LOW
TEMPERATURE DIFFERENTIAL SCANNING CALORIMETER (DSC)

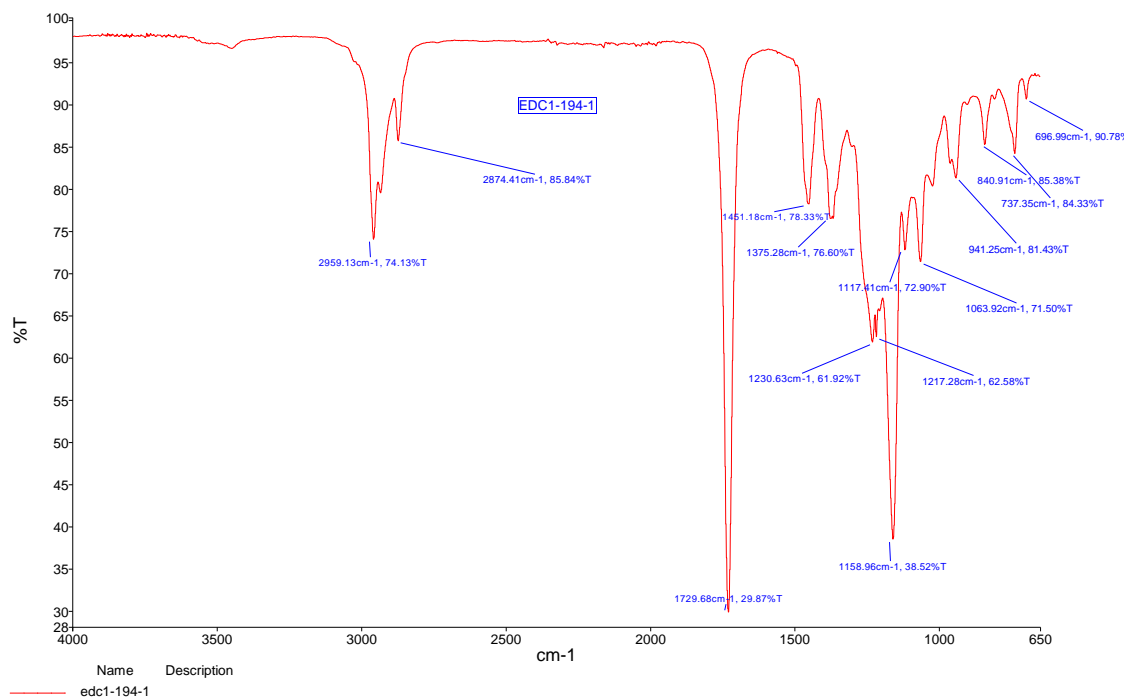


Figure A-1
FTIR spectra for co-polymer of butyl acrylate and 2-hydroxyethyl acrylate

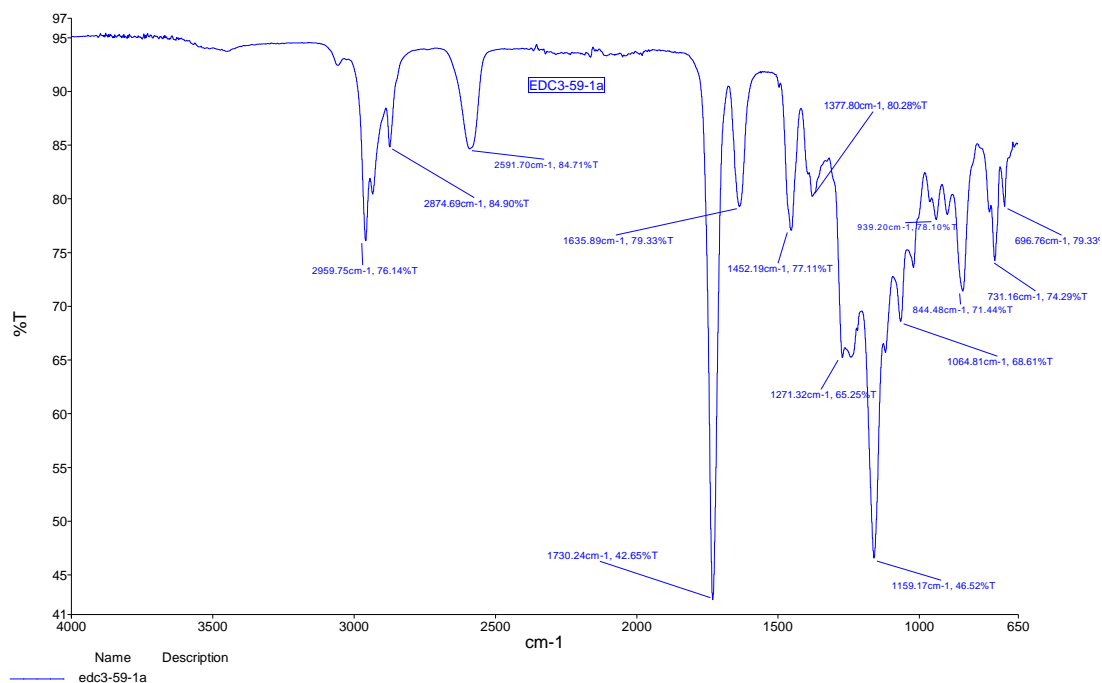


Figure A-2
FTIR spectra for co-polymer of butyl acrylate, 2-hydroxyethyl acrylate, and carboranymethyl acrylate

Co-polymerization was successful with the appearance of B-H stretching in the product FTIR spectra found at 2590 cm⁻¹.

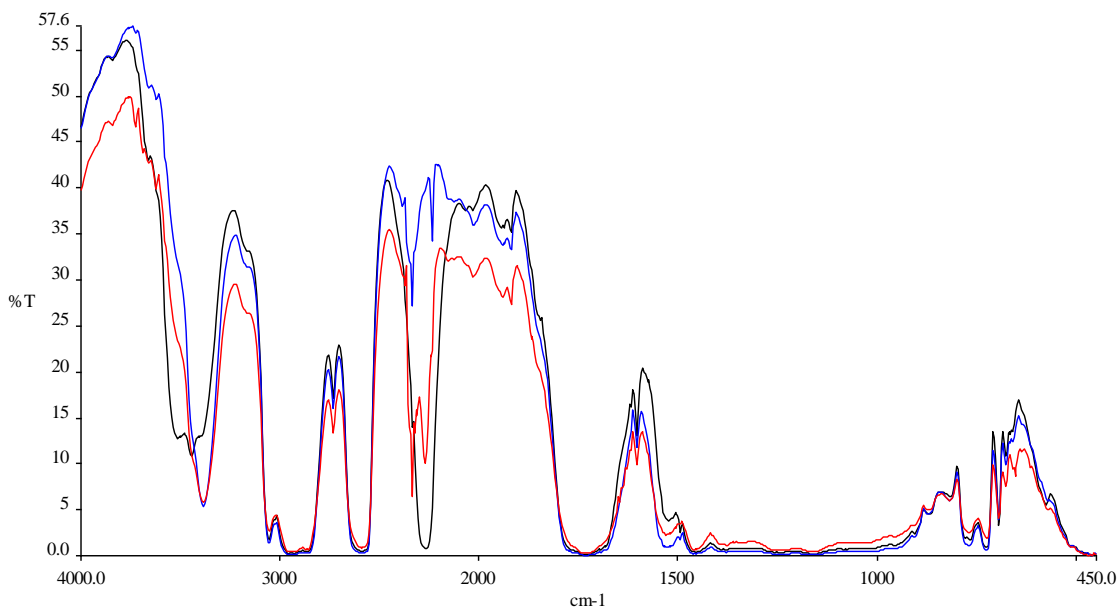


Figure A-3

Time elapsed FTIR spectra of co-polymer cross-linked with isocyanates (Black = 0 hours, Red = 1 hour, Blue = 15 hours). 3517 cm⁻¹ hydroxyl; 3057/2859 cm⁻¹ toluene and hydrocarbons; 2590 cm⁻¹ borane; 2271 isocyanate; 1732 cm⁻¹ acrylate; 1526 cm⁻¹ carbamate.

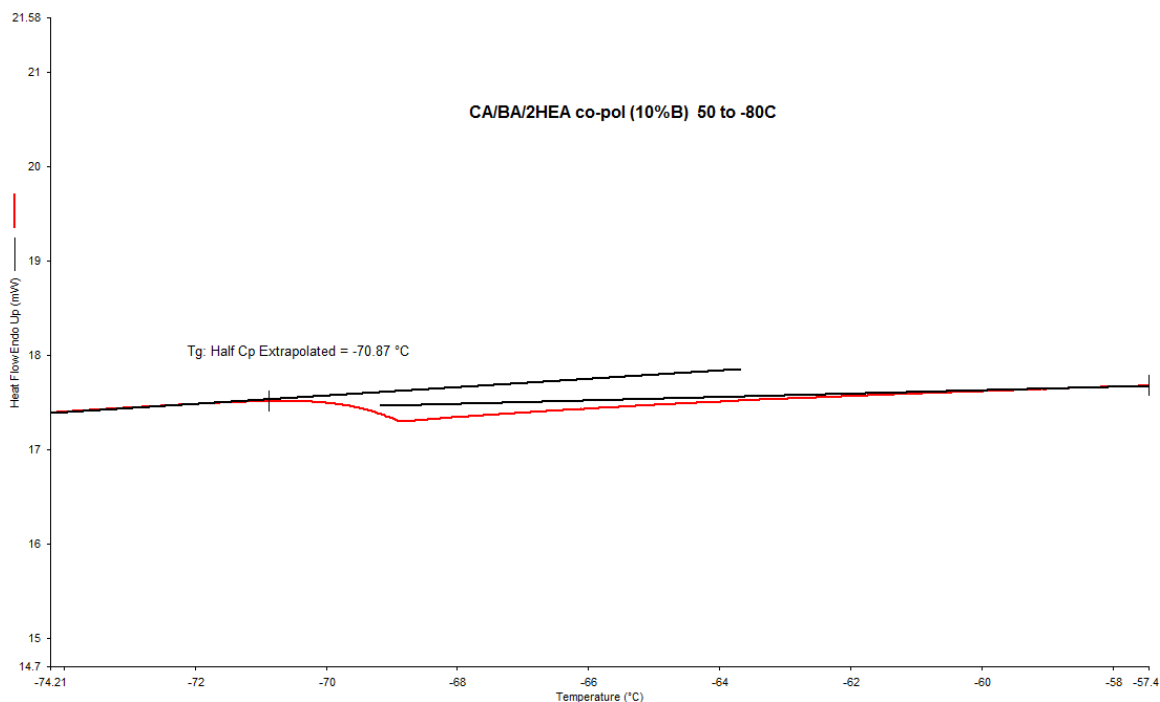


Figure A-4

Low temperature DSC spectra of Carboranymethyl acrylate/butyl acrylate/2-hydroxyethyl acrylate (10% Boron) co-polymer. Spectra indicates a T_g of -70.87 °C; well below room temperature and indicative of a free flowing polymer.

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APPENDIX B
FORMULATION VALUE TABLE, DIFFERENTIAL SCANNING CALORIMETER (DSC), AND BURN
RATE DATA

Table B-1

Designed formulation values for burn rate sticks. HTPB: hydroxyl terminated polybutadiene; ACR: polyacrylate; C-ACR: carboranypolyacrylate.

Ingredient	Function	Weight %
HTPB/ACR/C-ACR	Polymer/binder	11.4
DOA	Plasticizer	8.00
AP (200 micron)	Oxidizer	54.6
AP (15-25 micron)	Oxidizer	18.2
Aluminum (H30)	Fuel	7.27
IPDI	Curing Agent	0.508
DBTDL	Catalyst	0.072

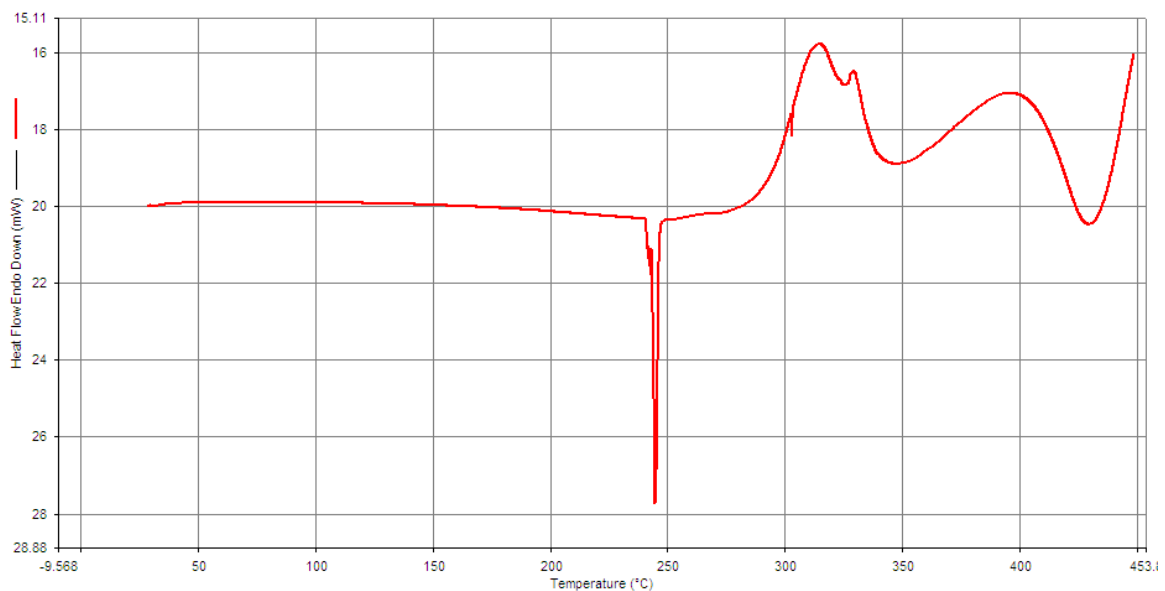


Figure B-2

DSC spectra of carboranymethyl acrylate containing formulation containing co-polymer, AP, and Aluminum. High temperature activity demonstrates stability of material.

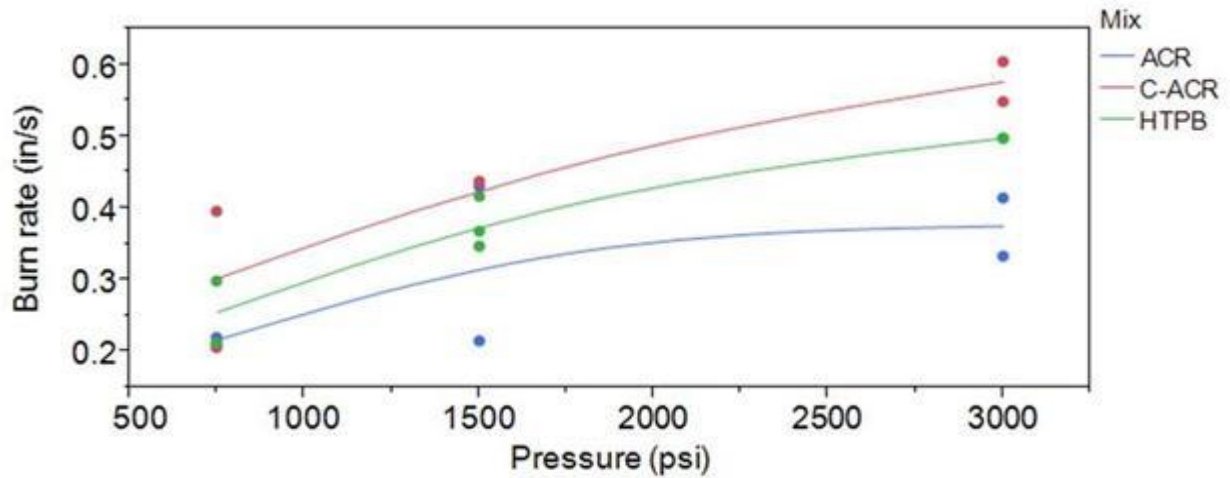


Figure B-3

Strand burn rate data gathered at three different pressures: 1000, 1500, 3000 psi. (ACR = Butyl acrylate/2-hydroxyethyl acrylate co-polymer (0% Boron); Carboranylmethyl acrylate/butyl acrylate/2-hydroxyethyl acrylate (10% Boron); HTPB = Hydroxy-terminated Polybutadiene)

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